Platinum nanoparticles as pH sensor for intelligent packaging

A. J. Martins, M. Benelmekki, V. Teixeira, P. J. G. Coutinho*
University of Minho, Centre of Physics, Campus de Gualtar, 4710-057 Braga, Portugal
email: pcoutinho@fisica.uminho.pt (corresponding author)

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Abstract.

Pt nanoparticles were produced by reverse micelle templating using DTAB. The resulting nanoparticles showes sizes between 250nm and 500nm and formed clusters. Thioglycolic acid (TGA) was covalently attached to the nanoparticle surface as a stabilizer and as. The Pt nanoparticles were dispersed in water and the dependence of its absorvance on the pH of the solution was studied. The spectra showed surface plamon absorption band at 280nm and also red shifted bands that were attributed to clusters of nanoparticles. It was found that the fraction of cluster population depends on the pH of the aqueous solution and that the response of the Pt nanoparticles to pH variations has a memory effect (hysteresis). The possibility of using these Pt nanoparticles in smart labels for food packaging is outlined.

Introduction

Intelligent packaging is part of a new class of packages that allows the monitoring of the conditions of its contents from the production line to the consumer.. All packages, that from centuries served to protect the food from microbial and chemical contamination, oxygen, water vapour and light and display information on the formation and characteristic of the food packaged, are now part of a class called passive packaging, being the most common the plastic bag. Recently, new classes of packaging have emerged (active and intelligent) due to consumer demands regarding food safety [1]. European Food Safety Authority (EFSA) states that active packaging interacts with food in order to improve shelf-life and packaged food conditions, while intelligent packaging monitors the food condition and/or the quality of packaged food or the surrounding environment. Intelligent packaging can be related to the inclusion of smart labels in the package that can give information on the physical-chemical properties, of the food or of the surroundings, like pH, temperature, [O_2], [CO_2]. In this work we explore the possibility of using platinum nanoparticles in a label that would monitor pH variations in packaged food products.

K.-S. Lee and M. A. El-Sayed reported that plasmonic metal nanoparticles have the right properties to be used as sensor, due to their sensitive spectral response to the surroundings of the nanoparticle surface[2]. Specifically, the surface plasmon resonance (SPR) absorption band that results from resonant coupling of incident light to the collective oscillation mode of conduction band electrons is very sensitive to the environment of the nanoparticle surface. Also the surface plasmon can enhance the emission quantum yield of molecules near to the metallic surface. This has been observed for Platinum both for fluorescence [3] and phosphorescence [4]. Platinum nanoparticles are thus good candidates for sensor applications either directly trough its SPR or indirectly through sensivity enhancement of molecular sensors that are based on fluorescence variations Platinum SPR absorption showed large variations with pH that had some hysteresis behaviour. The results show interesting effects that can lead to the use of these nanoparticles in smart food packaging labels as a temporary big pH change in the packaged food would induce a permanent effect on the sensor response.

Experimental

All reagents were of analytical grade and used as received.

We used the nanometric aqueous pools of water-in-oil (w/o) microemulsions (reverse micelles) of Dodecyl Trimethyl Ammonium Bromide (DTAB) in cyclohexane/pentanol as templates for the production of Pt nanoparticles through reduction of hexachloroplatinic acid by hydrazine. Equal volumes of two microemulsions are independently prepared by injecting aqueous solutions of either chlroroplatinic acid or NaOH basificated hydrazine monohydrate. These solutions are then added drop by drop and the reaction mixture is kept at 80ºC until a grey coloration appears. The final concentrations of Pt and hydrazine were 0.24mM and 3.6mM respectively. The solution was evaporated with nitrogen and the particles were washed and filtered several times with ethanol to remove the surfactant. In the case of Pt-TGA nanoparticles thioglycolic acid (TGA) was added to the reaction mixture after the grey color appeared.

Results and Discussion

Figure 1 shows the absorption spectrum of Pt-nanoparticles in the DTAB w/o microemulsion, after being cleaned and dispersed in water.

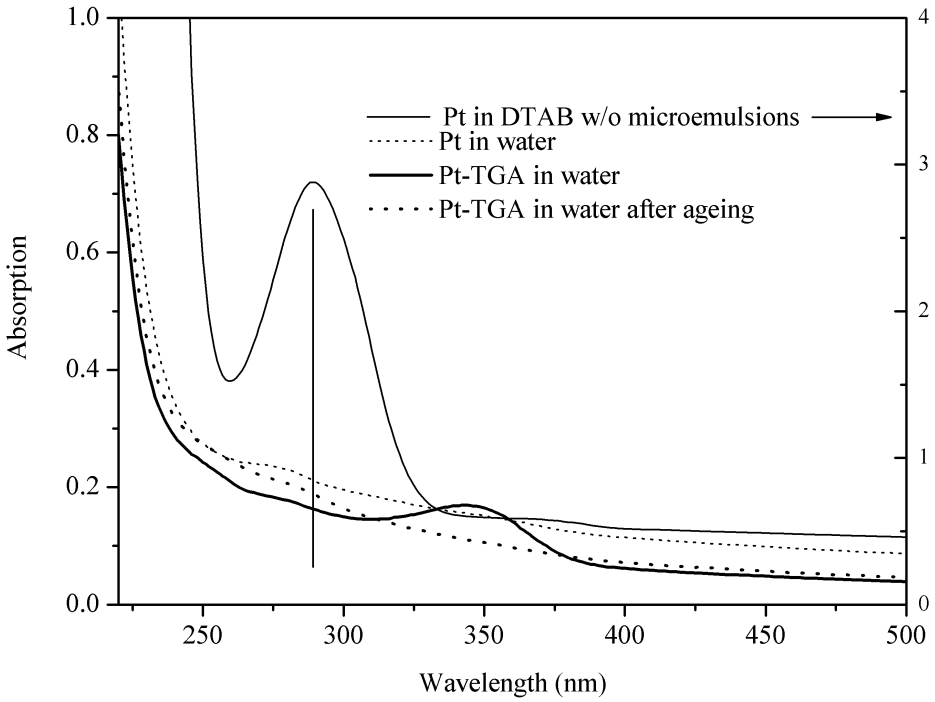

Figure 1: Absorption spectra of the Pt nanoparticles.

The characteristic Pt plasmon absorption band is observed near 290nm when the particles are covered by positively charged DTAB molecules and shifts 15nm to the blue with an intensity decrease when the particles are cleaned and dispersed in water. Theoretical calculation for 10nm spherical particles places the Pt plasmon band in the far UV (<200nm in vacuum and 215nm in

water with higher intensity) [5]. Those calculations used only the first term of the Mie expansion. This approximation fails when the size is above 20nm because higher multipole terms gain weight. The observed additional red shifted bands (fig. 1) can be assigned to clusters of Pt nanoparticles as a band at 537nm was recently reported for self-assembled Pt nanoparticles forming nanofibers [6]. In the case of TGA coated Pt nanoparticles those clusters almost disappear with ageing (~1 week storage). The size of the obtained particles was studied by STEM using the DTAB microemulsion (fig.2). Individual particles were spherical and showed sizes between 250nm and 500nm. Strong clustering of nanoparticles was also observed.

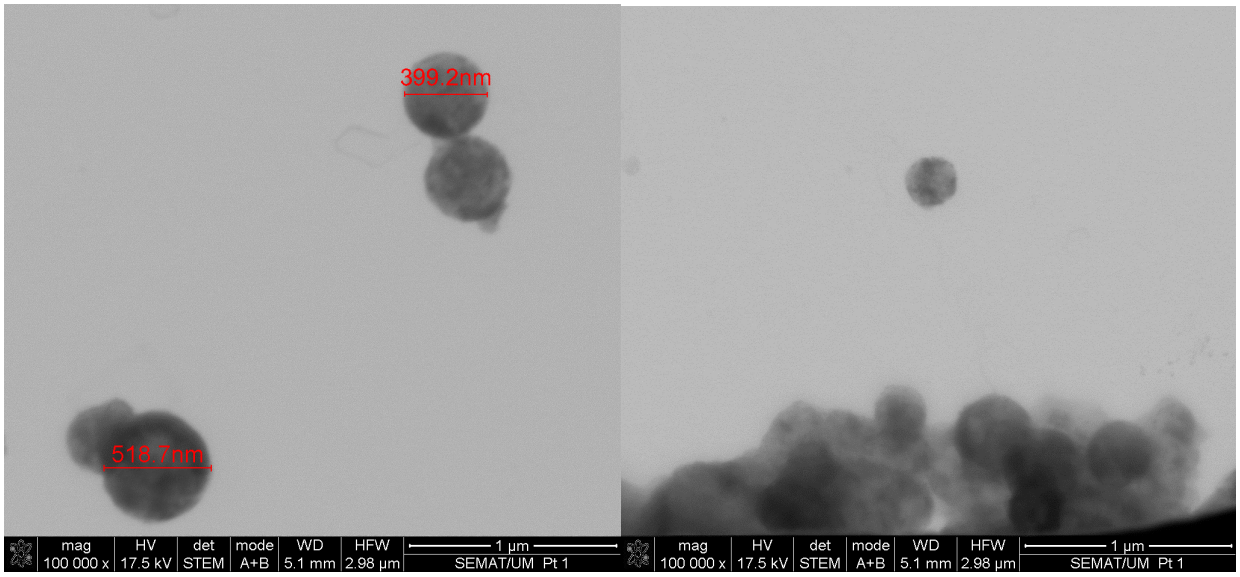

Figure 2: STEM imaging of Pt nanoparticles.

The pH of the water dispersion of Pt nanoparticles was varied by the addition of µl quantities of concentrated HCl or NaOH aqueous solutions. Figure 3 to 5 shows the pH response of the prepared dispersions of Pt in water. It is observed that the population of clusters increases with the solution pH as can be concluded from the rise in the absorption peak centered at 340nm and the corresponding decay in the 280nm region. Also some memory effect occurs that, with the exception of aged Pt-TGA, is mainly when pH comes back to 7 from acidic values. This memory effect always results in an absorption at the cluster region lower then expected. This can be interpreted by destabilization of clusters in acidic/basic media that reassemble upon neutralization but not into the same structure.

The memory effect is not a good characteristic when considering a straight pH measurement application. But, for the utilization in smart labels for food packaging, this is an interesting feature as a transient change of pH gets recorded in the Pt nanoparticles absorbance. It is only needed an additional control sensor that gives a reliable value of the actual pH of the solution. If absorbance values readed from the control and from the Pt-nanoparticles are different it would be possible to conclude that the food in the package underwent a significant pH change.

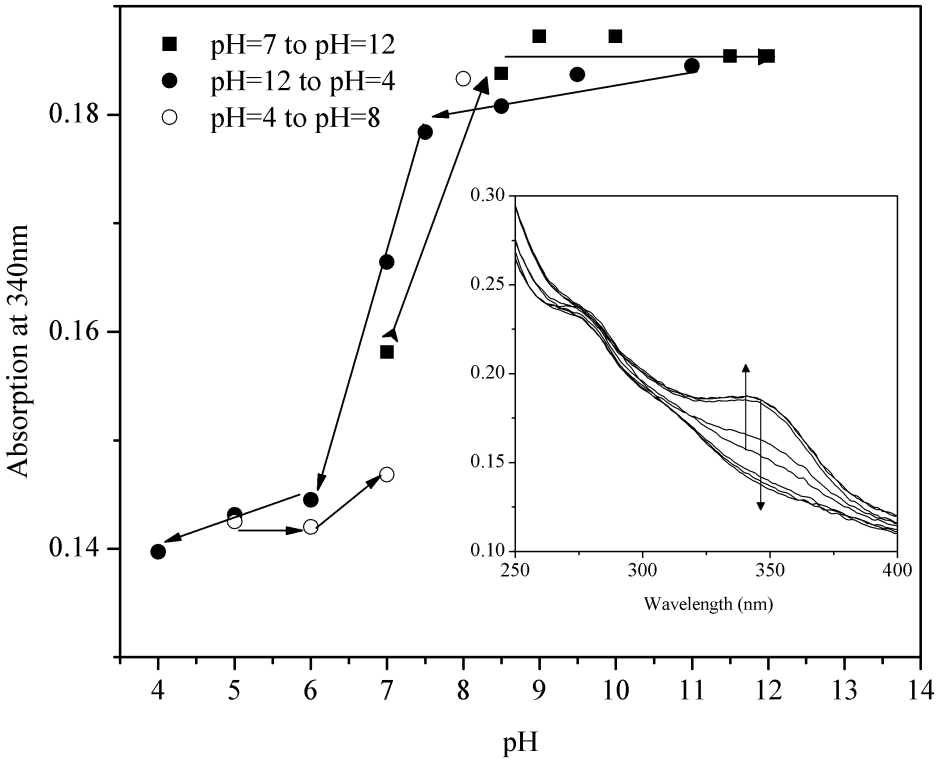

Figure 3: pH dependence of Pt nanoparticles dispersed in deionised water. The arrows indicate the sequence of pH variation.

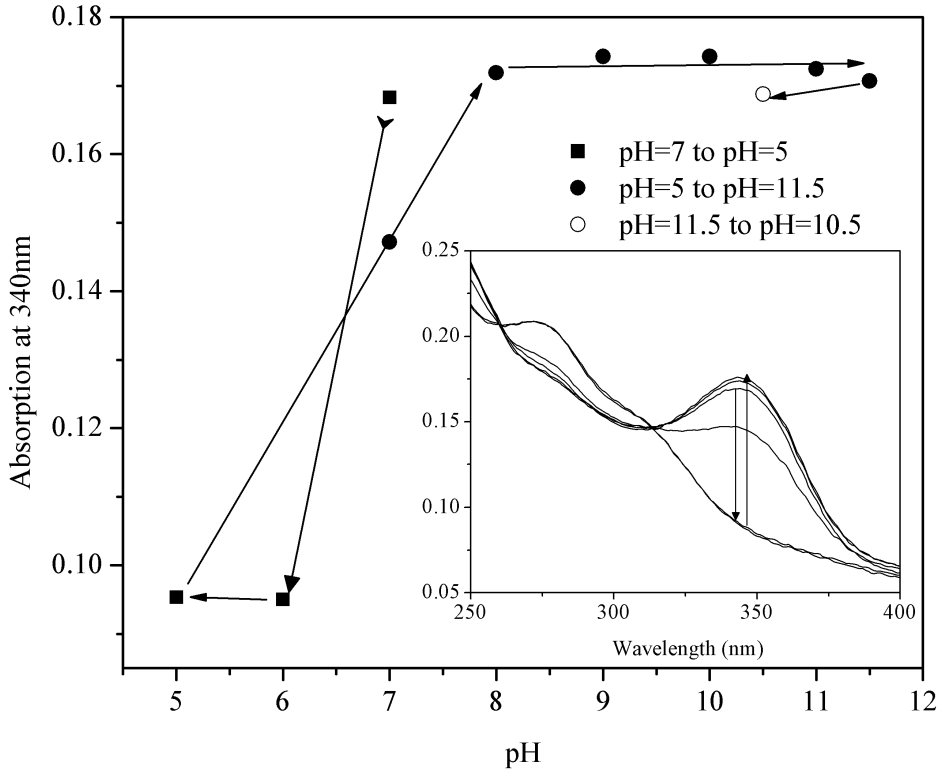

Figure 4: pH dependence of Pt-TGA nanoparticles dispersed in deionised water. The arrows indicate the sequence of pH variation.

It is interesting to note that the TGA molecules do not change significantly the pH at which the absorption shows a transition. For plain Pt nanoparticles this pH value is pH=7 and for the TGA coated ones a transition centered at pH 6.5 is observed. We were expecting for Pt-TGA a lower transition pH as the pKa of the carboxylic acid (the group that points to the exterior of the nanoparticle) is around 4.5. Also an enhanced presence of clusters in the Pt-TGA water dispersions can be a result of pairing of carboxylic groups from different nanoparticles.

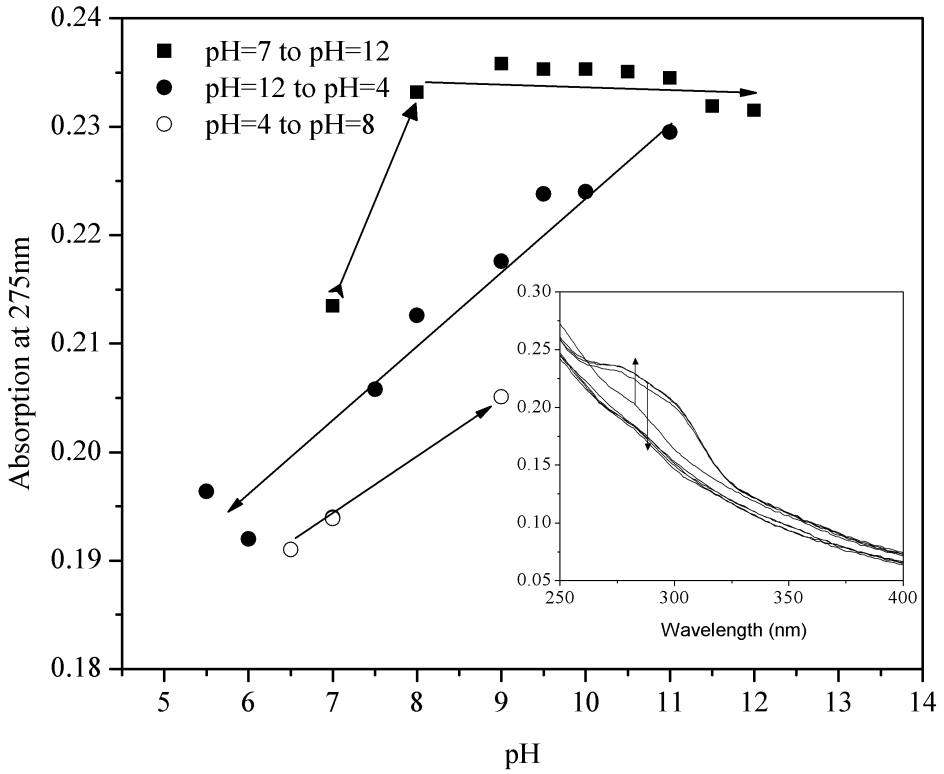

Figure 5: pH dependence of Pt-TGA nanoparticles dispersed in deionised water. The arrows indicate the sequence of pH variation.

The observed ageing effect of Pt-TGA nanoparticles in water dispersions can result from a slow equilibration between the various cluster types and isolated nanoparticles. The absorption band used for the pH result for the other Pt aqueous dispersions (fig. 3 and 4) is absent but a band at ~300nm appears in basic conditions. Following the absorption in the surface plasmon region (275nm) results in a more pronounced memory effect although the amplitude of variation is smaller.

Acknowledgements

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